



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB99/02151 (22) International Filing Date: 16 July 1999 (16.07.99) (30) Priority Data: 9816080.7 24 July 1998 (24.07.98) GB (71) Applicant (for all designated States except US): FOSECO INTERNATIONAL LIMITED [GB/GB]; Burmah Castrol House, Pipers Way, Swindon, Wiltshire SN3 1RE (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): STOETZEL, Reinhard [DE/DE]; Nonnenfettweide 20, D-46325 Borken (DE). STUHR, Helmut [DE/DE]; Wormlandstrasse 9, D-46325 Borken (DE). (74) Agent: LEWIS, Pauline, Therese; Burmah Castrol House, Pipers Way, Swindon, Wiltshire SN3 1RE (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COATING COMPOSITIONS		
(57) Abstract <p>A coating composition for use on sand cores and moulds in foundries is disclosed. The coating composition comprises particulate refractory material having a particle size of predominantly less than 150 microns, a binder, water and a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones. Also disclosed is a coating system comprising two or more separate parts to be mixed together to form a coating composition, the coating system comprising: (a) particulate refractory material having a particle size of predominantly less than 150 microns, and a binder; and, separately, (b) a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones. The water soluble or water miscible additive may comprise one or more of: diacetin, triacetin, butylene glycol diacetate, propylene carbonate, gamma-butyrolactone, for example.</p>		

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COATING COMPOSITIONS

This invention relates to coating compositions for use on sand cores and moulds in foundries.

It is common practice in foundries to coat sand cores and moulds with a coating of fine particle size refractory material, in order to prevent penetration of molten metal into the surface of the core or mould between the sand grains, and in the case of silica sand cores and moulds used for casting iron, to prevent reaction between the silica and iron oxide and adhesion between the sand and the cast metal, and thereby to improve the surface finish of metal cast against the cores or moulds. The coatings are usually applied in the form of a dispersion of the particulate refractory material in a liquid medium, which also contains a binder for the refractory particles. The liquid medium is usually water or an organic liquid such as isopropanol.

One of the numerous binders which are used to make foundry sand cores and moulds is an aqueous solution of sodium silicate, which is reacted with carbon dioxide gas passed through the cores or moulds so as to cure the silicate and bond the sand grains together. Cores and moulds which have been bonded with sodium silicate suffer from the disadvantage that when a water based coating is applied to the cores and moulds their surface is disintegrated and they are softened, thus reducing their strength appreciably, due to dissolution of the sodium silicate bond by the water. In some instance it is possible to use a water based coating on sodium silicate bonded cores provided the coating is dried immediately after it has been applied, but this usually involves installing a continuous drying oven in the foundry. However, in most foundries making sodium silicate bonded cores and moulds it is normal practice to coat the cores and moulds with an alcohol based coating. For safety and for environmental reasons it is desirable to replace the alcohol based coatings with water based coatings, but

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without the need to provide means for drying the coatings as soon as they have been applied.

It has now been found that a water based coating can be used successfully on carbon dioxide gassed sodium silicate bonded cores and moulds if the coating composition used contains a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones.

According to a first aspect of the present invention there is provided a coating composition comprising particulate refractory material having a particle size of predominantly less than 150 microns, a binder, water and a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones.

According to a second aspect, the invention provides a coating system comprising two or more separate parts to be mixed together to form a coating composition, the coating system comprising:

- (a) particulate refractory material having a particle size of predominantly less than 150 microns, and a binder; and, separately,
- (b) a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones.

The separate parts of the coating system are preferably mixed together substantially immediately before coating is to be carried out. Water is preferably added to the coating system, for example at the same time as the separate parts are mixed together.

According to a third aspect, the invention provides a method of forming a coating composition, comprising mixing together:

- (a) particulate refractory material having a particle size of predominantly less than 150 microns, and a binder;

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- (b) a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones; and
- (c) water.

The particulate refractory material may be for example, one or more of zircon, alumina, chromite, silica, talc, olivine, graphite, an aluminosilicate such as calcined clay, pyrophyllite and mica.

The binder may be for example solution or dispersion of a polyacrylate, a solution or dispersion of polyvinyl alcohol, dextrin, starch. The binder should be one which will not react with the polyhydric alcohol ester, carbonate ester or lactone. Binders which should not be used because they would react with the polyhydric alcohol ester, carbonate ester or lactone include alkali metal silicates and alkaline resol phenol-formaldehyde resins.

The water soluble or water miscible additive may be for example diacetin, triacetin, butylene glycol diacetate, propylene carbonate, or gamma-butyrolactone. Industrial grade diacetin (glycerol diacetate) is preferred.

The coating composition may also contain other components, for example, a suspension agent to prevent settling of the particulate refractory material, for example a clay such as attapulgite or bentonite or a rheological agent to improve the application properties of coating composition such as a cellulose derivative, a flocculant or a dispersant.

The coating composition (and when formed from the coating system, the water diluted coating composition) will usually contain at least 0.5%, preferably at least 1.0%, more preferably at least 2.0% especially at least 4.0% by weight of the water soluble or water miscible additive. Preferably the composition contains no more than 20.0%, more preferably no more than 15.0%, especially no more than 10.0% by weight of the water soluble or water miscible additive. The actual

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amount of the additive used may depend on the method of application of the coating composition to the cores or moulds.

The coating composition may be applied by any of the usual methods used in foundries, for example by brushing, dipping, spraying or overpouring. The solids content of the coating composition will depend on the method of application, but will usually be a maximum of 75% by weight.

The coating compositions of the invention are particularly advantageous when used on carbon dioxide gassed sodium silicate bonded sands. However they can also be used beneficially on other types of bonded sand which may have a tendency to soften and disintegrate when conventional water based coating compositions are applied to them. These sands include carbon dioxide gassed alkaline resol phenol-formaldehyde resin bonded sand, ester hardened sodium silicate bonded sand, and ester cured alkaline resol phenol-formaldehyde resin bonded sand.

The following Examples will serve to illustrate the invention :-

EXAMPLE 1

Standard transverse strength test cores were produced from H 32 silica sand containing 3.5 % by weight of a proprietary sodium silicate binder, NUCLEOPON 20, available from Foseco (silica to soda molar ratio 2.4 : 1 and solids content 49 % by weight).

Three proprietary water based coating compositions available from Foseco, TERRAPAIN EP 9828 AT (composition 1), RHEOTEC 463 BW

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(composition 2) and HOLCOTE 90 (composition 3), were diluted to a dipping consistency with water, and 5 % by weight of commercial diacetin based on the weight of the diluted coated composition were added to produce coating compositions according to the invention.

The coating compositions were applied to the standard transverse strength test cores by dipping, and transverse strengths were measured immediately after application of the coating (while wet), one hour after drying at 120 °C for 30 minutes, and after 24 hours.

Similar tests were done on specimens which had been coated with coating composition 4, a proprietary alcohol based coating, MOLCO 6, available from Foseco.

The results obtained are shown in the table below.

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COATING COMPOSITION	TRANSVERSE STRENGTH (N/cm ²)		
	Immediately	After 1 hour	After 24 hours
1	50	133	115
1	60	157	130
2	70	105	99
2	70	96	115
3	60	145	120
3	70	131	132
4	70	70	54
4	70	82	61

The results show that the strength of the cores after immediately coating with each of the three compositions according to the invention was comparable to that of cores which had been coated with the alcohol based coating which is of the type normally used for coating sodium silicate bonded cores. After drying for 1 hour the strength of the cores coated with the compositions according to the invention was appreciably higher than both the strength immediately after application, and the strength of the cores coated with the alcohol based coating. After 24 hours the appreciable improvement was maintained.

EXAMPLE 2

120 kg of silica sand were mixed with 3.6% by weight based on the weight of the sand of SOLOSIL 433, a proprietary sodium silicate based binder available from Foseco of the type described in European Patent No. 0024392. Housing cores were made from the sand-binder mixture by core-shooting at a pressure 6 bars and by gassing the formed cores with carbon dioxide gas at a pressure of 5 bars for 15 seconds.

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A proprietary water-based coating zircon composition RHEOTEC 300 available from Foseco containing an addition of 10% by weight of diacetin based on the weight of the composition as supplied, and having a density of 70° Baumé, was diluted with water in the proportions 150 kg of the coating composition containing the diacetin additive and 40 kg water. The diluted coating composition had a density of 42° Baumé and a viscosity of 13.5 seconds as measured on a Ford Cup No. 4.

The housing cores were dipped into the coating composition so as to produce a wet coating thickness of approximately 175 microns. The coated cores were held for a maximum of 15 minutes dried in a microwave drying unit. After drying for 10 minutes the cores were still wet and had a surface temperature of 55° to 60° C. The cores were then dried for a further 15 minutes after which time they were almost completely dry and had a surface temperature of 60° to 70° C. The cores were then inspected, and they showed no signs of having been affected adversely by the water based coating.

In contrast, in a comparison test using similar cores coated with a water-based aluminosilicate coating ARCOPAL 6423 (available from Hüttenes-Albertus) the coated cores had started to disintegrate.

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Claims

1. A coating composition, comprising particulate refractory material having a particle size of predominantly less than 150 microns, a binder, water and a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones.
2. A coating system comprising two or more separate parts to be mixed together to form a coating composition, the coating system comprising:
 - (a) particulate refractory material having a particle size of predominantly less than 150 microns, and a binder; and, separately,
 - (b) a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones.
3. A coating system according to Claim 2, further comprising water.
4. A method of forming a coating composition, comprising mixing together:
 - (a) particulate refractory material having a particle size of predominantly less than 150 microns, and a binder;
 - (b) a water soluble or water miscible additive selected from esters of polyhydric alcohols, carbonate esters and lactones; and
 - (c) water.
5. A composition, system or method according to any preceding claim, in which the particulate refractory material comprises one or more of: zircon, alumina, chromite, silica, talc, olivine, graphite, an aluminosilicate.
6. A composition, system or method according to any preceding claim, in which the binder comprises a solution or dispersion of a polyacrylate.

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7. A composition, system or method according to any preceding claim, in which the binder comprises polyvinyl alcohol.
8. A composition, system or method according to any preceding claim, in which the binder comprises dextrin and/or starch.
9. A composition, system or method according to any preceding claim, in which the water soluble or water miscible additive comprises one or more of: diacetin, triacetin, butylene glycol diacetate, propylene carbonate, gamma-butyrolactone.
10. A composition, system or method according to any preceding claim, in which the ready for use coating composition contains at least 0.5%, preferably at least 1.0%, more preferably at least 2.0% especially at least 4.0% by weight of the water soluble or water miscible additive.
11. A composition, system or method according to any preceding claim, in which the ready for use coating composition contains no more than 20.0%, more preferably no more than 15.0%, especially no more than 10.0% by weight of the water soluble or water miscible additive.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02151

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B22C3/00 B22C1/02 C09D5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B22C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 202 004 A (FOSECO INT) 20 November 1986 (1986-11-20) whole document	1-11
A	----- DATABASE WPI Section Ch, Week 198809 Derwent Publications Ltd., London, GB; Class M22, AN 1988-062351 XP002122558 & SU 1 324 743 A (KALUGA MECH ENG), 23 July 1987 (1987-07-23) abstract -----	1-11



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

12 November 1999

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Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02151

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0202004 A	20-11-1986	BR 8601722 A ES 554149 A JP 61242972 A	16-12-1986 01-04-1988 29-10-1986
SU 1324743 A	23-07-1987	NONE	

DERWENT-ACC-NO: 2000-223738**DERWENT-WEEK:** 200444*COPYRIGHT 2008 DERWENT INFORMATION LTD*

TITLE: Coating composition for use on sand
cores and molds in foundries e.g.
carbon dioxide gassed sodium silicate
bonded cores and molds

INVENTOR: STOETZEL R; STUHR H**PATENT-ASSIGNEE:** FOSECO INT LTD[FOSE]**PRIORITY-DATA:** 1998GB-016080 (July 24, 1998)**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
WO 0005010 A1	February 3, 2000	EN
AU 9950475 A	February 14, 2000	EN
EP 1113890 A1	July 11, 2001	EN
BR 9912379 A	October 2, 2001	PT
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MX 2001000813 A1	September 1, 2001	ES
EP 1113890 B1	December 10, 2003	EN
DE 69913539 E	January 22, 2004	DE
ES 2211128 T3	July 1, 2004	ES

DESIGNATED-STATES: AE AL AM AT AU AZ BA BB BG BR BY
 CA CH CN CU CZ DE DK EE ES FI GB
 GD GE GH GM HR HU ID IL IN IS JP
 KE KG KP KR KZ LC LK LR LS LT LU
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 DE DK ES FI FR GB GR IE IT LI LT
 LU LV MC MK NL PT RO SE SI AL AT
 BE CH CY DE DK ES FI FR GB GR IE
 IT LI LT LU LV MC MK NL PT RO SE SI

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2000005010A1	N/A	1999WO- GB02151	July 16, 1999
AU 9950475A	N/A	1999AU- 050475	July 16, 1999
BR 9912379A	N/A	1999BR- 012379	July 16, 1999
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EP 1113890B1	N/A	1999EP- 934828	July 16, 1999
EP 1113890A1	N/A	1999WO- GB02151	July 16, 1999
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EP 1113890B1	N/A	1999WO- GB02151	July 16, 1999

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KR2001071014A	N/A	2001KR- 700949	January 22, 2001
MX2001000813A1	Based on	2001MX- 000813	January 23, 2001

INT-CL-CURRENT:

TYPE	IPC DATE
CIPS	B22C3/00 20060101
CIPS	C09D5/02 20060101

ABSTRACTED-PUB-NO: WO 0005010 A1**BASIC-ABSTRACT:**

NOVELTY - Coating composition comprises particulate refractory material having a particle size of less than 150 microns; a binder; water; and a water soluble or water miscible additive including esters of polyhydric alcohols, carbonate esters, or lactones.

DESCRIPTION - INDEPENDENT CLAIMS are also included for:

(I) a coating system comprising (a) particulate refractory material having a particle size less than 150 microns and a binder, and separately, (b) a water soluble or water miscible additive including esters of polyhydric alcohols, carbonate esters, or lactones; and

(II) a method of forming the coating composition, which comprises mixing of the components.

USE - The coating compositions are used on sand cores and molds in foundries, particularly on carbon dioxide gassed sodium silicate bonded cores and molds. It can also be used on carbon dioxide gassed alkaline resol phenol-formaldehyde resin bonded sand, ester hardened sodium silicate bonded sand, and ester cured alkaline resol phenol-formaldehyde resin bonded sand.

ADVANTAGE - The composition is a water-based coating and is used successfully on carbon dioxide gassed sodium silicate bonded cores and molds without an additional drying process. The use of alcohol-based coatings are avoided. The cores coated with the invented composition exhibited superior strength.

EQUIVALENT-ABSTRACTS:

INORGANIC CHEMISTRY

Preferred Material: The particulate refractory material comprises at least one of zircon, alumina, chromite, silica, talc, olivine, graphite and an aluminosilicate.

POLYMERS

Preferred Binder: The binder comprises a polyacrylate solution or dispersion, polyvinyl alcohol, dextrin, and/or starch.

ORGANIC CHEMISTRY

Preferred Additive: The water soluble or water miscible additive comprises at least one of diacetin, triacetin, butylene glycol diacetate, propylene carbonate, and gamma-butyrolactone. Preferred Composition: The ready for use coating composition contains at least 0.5, preferably at least 4.0 wt.%; or contains no more than 20.0, preferably no more than

10.0 wt.% water soluble or water miscible additive.

Standard transverse strength test cores were produced from H 32 silica sand containing 3.5 wt.% NUCLEOPON 20 sodium silicate binder. Water-based coating compositions of TERRAPANT EP 9828 AT, RHEOTEC 463 BW, and HOLCOTE 90 were diluted with water, and 5 wt.% diacetin based on the weight of the diluted coated composition were added to produce a coating composition which was applied to the standard transverse strength (N/cm²) test cores by dipping. Transverse strengths were measured immediately after application, 1 hour after drying at 120 degrees C for 30 min, and after 24 hours. Similar test was done on a specimens which had been coated with an alcohol-based coating composition. The results showed that the strength of the cores immediately after coating, and after drying for 1 and 24 h were the same to and higher than that of cores coated with the alcohol-based coating, respectively.

TITLE-TERMS: COATING COMPOSITION SAND CORE FOUNDRY
CARBON GAS SODIUM SILICATE BOND

DERWENT-CLASS: A82 E17 G02 M22 P53

CPI-CODES: A12-A02; E07-A02; E07-A03; E07-A04;
E10-A11B2; E10-E04K; E10-G02G2; E31-
N04B; E31-P02D; E31-P03; E31-P05; E34-
C02; E35-P; G02-A05; M22-A04;

CHEMICAL-CODES: Chemical Indexing M3 *01*
Fragmentation Code A540 A940 B114
B713 B720 B831 C108 C802 C803 C804
C805 C807 M411 M782 Q130 Q332 Q466
R024 R043 Specific Compounds R04923
Registry Numbers 130252

Chemical Indexing M3 *02*
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C807 M411 M782 Q130 Q332 Q466 R024
R043 Specific Compounds R01544
Registry Numbers 130157 92

Chemical Indexing M3 *03*
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C807 M411 M782 Q130 Q332 Q466 R024
R043 Specific Compounds R01933
Registry Numbers 129802 130432 130898
853

Chemical Indexing M3 *04*
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R043 Specific Compounds R01694
Registry Numbers 107016

Chemical Indexing M3 *05*
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R01541 RA01JR Registry Numbers 108296
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Chemical Indexing M3 *06*
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Specific Compounds R01778 Registry
Numbers 200703

Chemical Indexing M3 *07*
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Registry Numbers 135365

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J011 J1 J171 M210 M212 M262 M281 M320
M423 M510 M520 M530 M540 M782 Q332
Q466 R024 R043 Specific Compounds
RA02L0 RA037T Registry Numbers 104380
199392

Chemical Indexing M3 *10*
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H713 H721 H8 M210 M212 M272 M281 M320
M423 M510 M520 M530 M540 M782 Q332
Q466 R024 R043 Specific Compounds
RA01EA Registry Numbers 104492

Chemical Indexing M3 *11*
Fragmentation Code M423 M782 Q332
Q466 R024 R043 Specific Compounds
R03275 Registry Numbers 92830

Chemical Indexing M3 *12*

Fragmentation Code M423 M782 Q332
Q466 R024 R043 Specific Compounds
R01863 Registry Numbers 107779

Chemical Indexing M3 *13*
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J012 J2 J272 M210 M211 M262 M282 M313
M321 M332 M343 M383 M391 M416 M620
M782 Q130 Q332 Q466 R024 R043
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Numbers 92859

Chemical Indexing M3 *14*
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Chemical Indexing M3 *15*
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Q332 Q466 R024 R043 Specific
Compounds R00844 Registry Numbers
1956

Chemical Indexing M3 *16*
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M540 M782 Q130 Q332 Q466 R024 R043
Specific Compounds R00644 Registry
Numbers 780

Chemical Indexing M3 *17*
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M210 M212 M272 M282 M314 M321 M331
M342 M382 M391 M416 M620 M782 Q130

Q332 Q466 R024 R043 Specific
Compounds RA0Z9M Registry Numbers
246935

Chemical Indexing M3 *18*
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J013 J014 J2 J272 J273 L630 L660 L699
M210 M211 M212 M213 M214 M215 M216
M220 M221 M222 M223 M224 M225 M226
M231 M232 M233 M262 M282 M283 M311
M312 M313 M314 M315 M316 M321 M331
M332 M333 M334 M340 M342 M343 M344
M383 M391 M416 M620 M782 Q130 Q332
Q466 R024 R043 Markush Compounds
001453601

**UNLINKED-DERWENT-REGISTRY-
NUMBERS:**

; 0644U ; 0744U ;
0844U ; 1541U ; 1544U ;
1694U ; 1863U ; 1933U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]
018 ; G0340*R G0339
G0260 G0022 D01 D12 D10
D26 D51 D53 D58 D63 F41
F89; H0000; H0011*R;
S9999 S1025 S1014;
S9999 S1616 S1605;
P0088;

Polymer Index [1.2]
018 ; P1707 P1694 D01;
S9999 S1025 S1014;
S9999 S1616 S1605;

Polymer Index [1.3]
018 ; D01 D11 D10 D23
D22 D31 D42 D50 D76 D86
F24 F29 F26 F34 H0293
M2313 P0599 G3623

R03275 R01863 107779
92830; S9999 S1025
S1014; S9999 S1616
S1605;

Polymer Index [1.4]
018 ; D01 D11 D10 D23
D22 D31 D42 D50 D76 D86
F24 F29 F26 F34 H0293
P0599 G3623 R01863
107779; S9999 S1025
S1014; S9999 S1616
S1605;

Polymer Index [1.5]
018 ; Q9999 Q7114*R;
K9712 K9676; ND01;
Q9999 Q6791; Q9999
Q7943 Q7885; K9574
K9483; K9610 K9483;
K9676*R; B9999 B4091*R
B3838 B3747;

Polymer Index [1.6]
018 ; G2335 D00 F20 H*
O* 6A R01740 3; A999
A475;

Polymer Index [2.1]
018 ; G1105 G1092 D01
D19 D18 D31 D50 D76 D86
F31 F30 R00868 181;
G1503 D01 D50 D81 F22
R00001 34; H0022 H0011;
P0226 P0282*R D01 D18
F30; P0293;

Polymer Index [2.2]
018 ; B9999 B5436 B5414

B5403 B5276; B9999
B5447 B5414 B5403
B5276; ND01; Q9999
Q6791; Q9999 Q7943
Q7885; K9574 K9483;
K9610 K9483; K9676*R;
B9999 B4091*R B3838
B3747;

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